Fourth Annual Conference on Carbon Capture & Sequestration

Developing Potential Paths Forward Based on the Knowledge, Science and Experience to Date

Advanced Conversion/Capture Concepts

Exploring the Potential to Enhance Aqueous Olivine Carbonation Reactivity, While Avoiding the Cost of Mineral Pretreatment Activation

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EXPLORING THE POTENTIAL TO ENHANCE AQUEOUS OLIVINE CARBONATION REACTIVITY, WHILE AVOIDING THE COST OF MINERAL PRETREATMENT ACTIVATION

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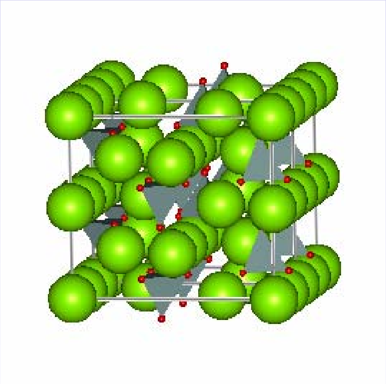

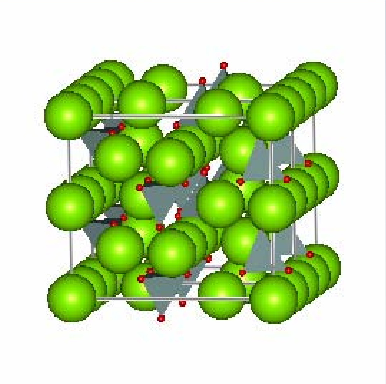

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CARBON DIOXIDE SEQUESTRATION VIA Mg-RICH MINERAL CARBONATION

ADVANTAGES

- **The process occurs naturally and yields *environmentally benign and geologically stable products* (e.g., $MgCO_3$ and SiO_2).**
- **It offers the capacity for *large scale sequestration*. Mg-rich minerals are widely available globally as relatively *low cost feedstocks* (e.g., olivine and serpentine).**
- **It *minimizes the ongoing costs* associated with long term storage (e.g., site monitoring, leakage, liability, etc.).**
- ***Carbonation is exothermic* for both serpentine and olivine, enhancing the potential for low-cost process development.**

PRIMARY CHALLENGE

Economically viable process development.

AQUEOUS SOLUTION MINERAL CARBONATION

$$\underset{\textit{olivine}}{Mg_2SiO_4} + 2CO_2 \xrightarrow[0.64\ M\ NaHCO_3 + 1M\ NaCl]{\sim 185\ ^oC,\ \sim 150\ atm\ CO_2} 2MgCO_3 + SiO_2$$

<u>An Intriguing Process</u>

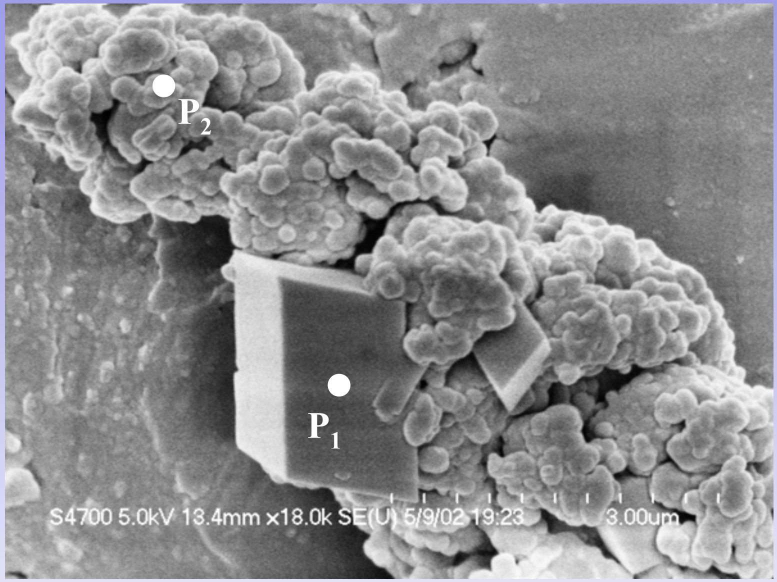
- **Developed by the Albany Research Center (ARC).**
- **Accelerated Mg-rich mineral carbonation from geological time to < 1 hour via heat and mechanical feedstock activation.**

<u>The Primary Challenge</u>

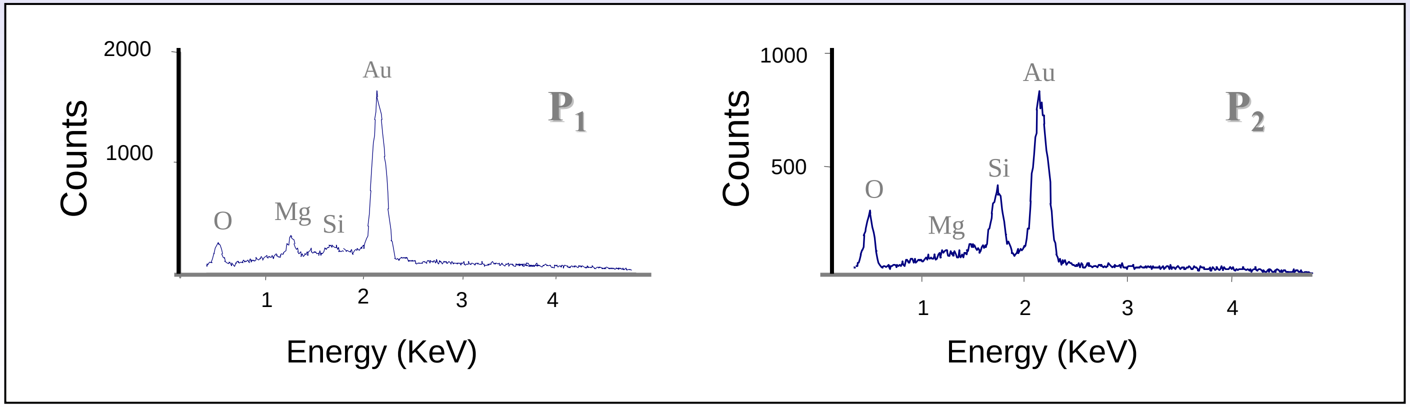
- **Reducing Process Cost**

  In particular, *reducing or eliminating the cost of mineral activation*, while enhancing carbonation.

DEVELOPING A MECHANISTIC UNDERSTANDING OF OLIVINE MINERAL CARBONATION

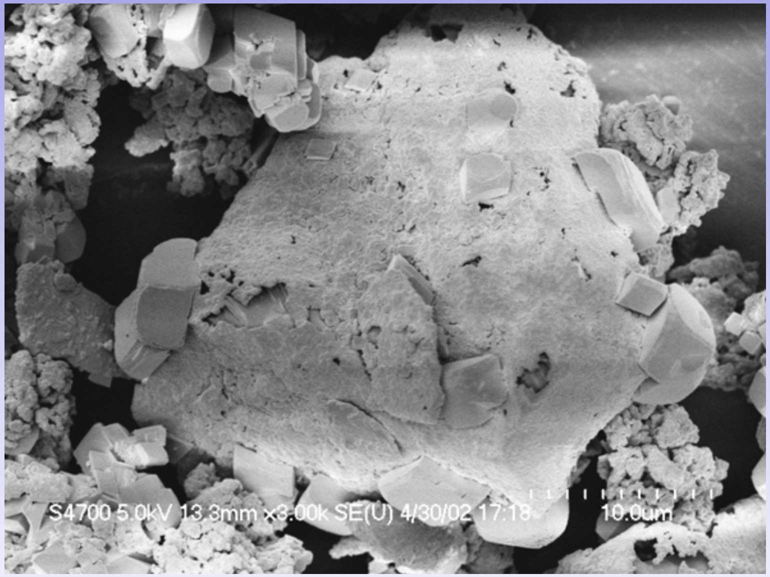


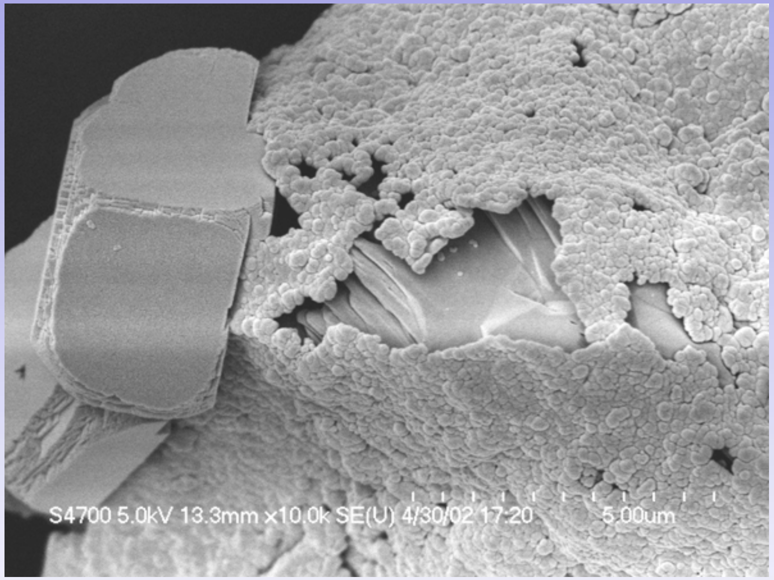
*1,500 rpm stirring



FESEM/EDS analysis of San Carlos olivine carbonation products

SILICA-RICH PASSIVATING LAYER FORMATION AND MAGNESITE INTERGROWTH*

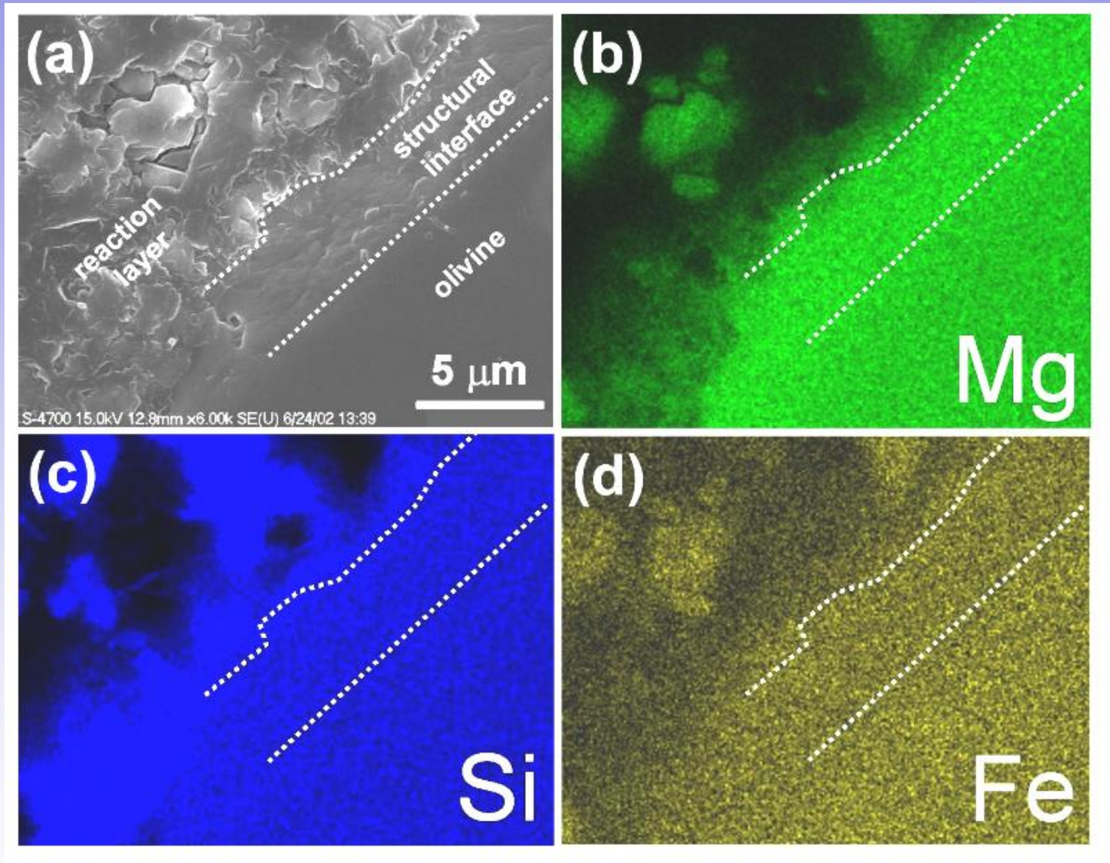




Note the substantial abrasion of the external magnesite crystal edges associated with the partially carbonated olivine reaction matrix

***1,500 rpm stirring**

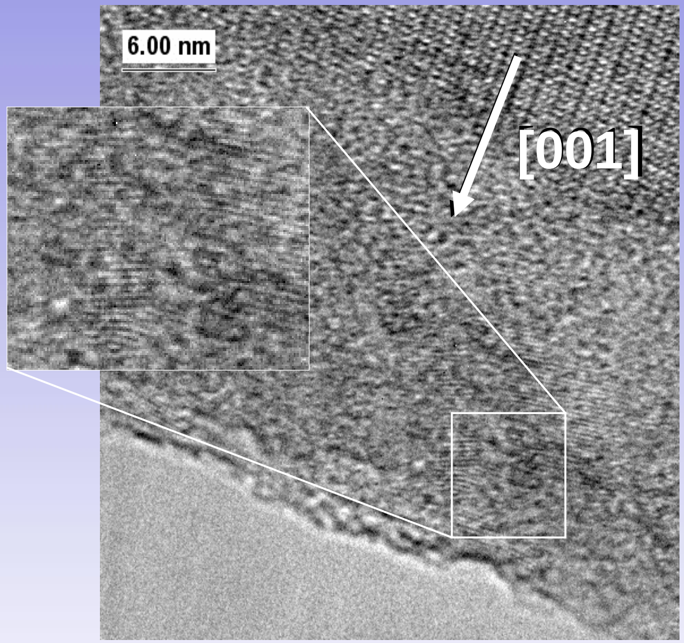
STRUCTURAL DISRUPTION PRECEDES CARBONATION INTO THE OLIVINE PARTICLE CORE*



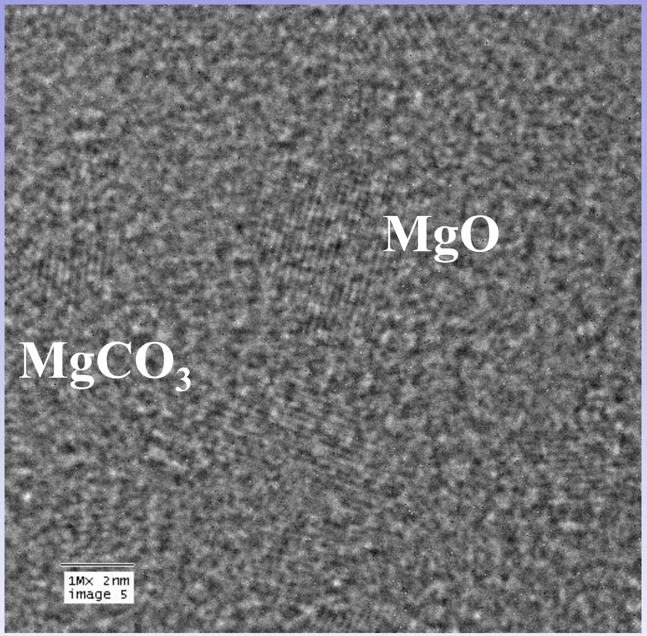
San Carlos olivine feedstock: $(Mg_{0.92}Fe_{0.08})_2SiO_4$

***1,500 rpm stirring**

MAGNESITE NANOCRYSTALS FORM IN THE SILICA-RICH PASSIVATING LAYERS*



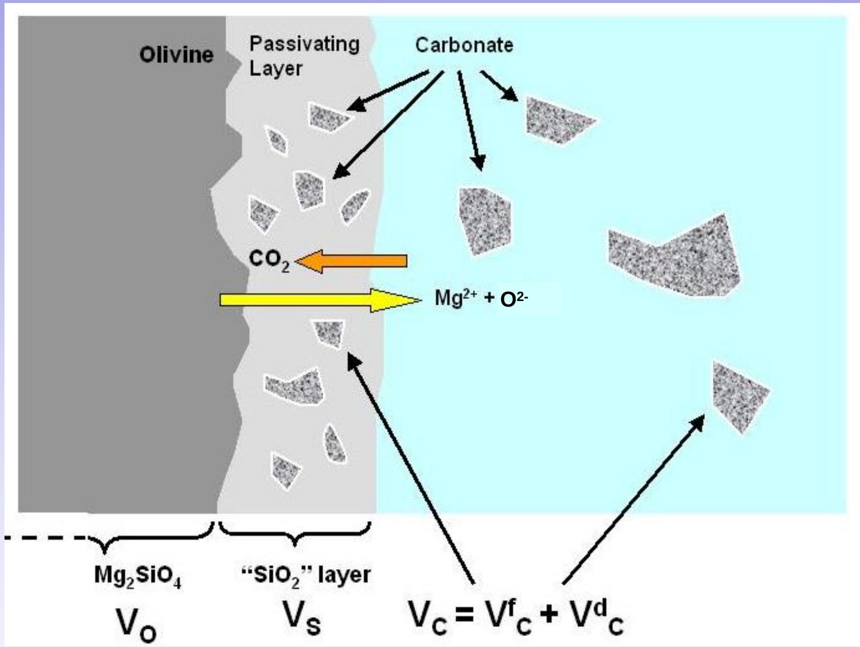
A high-resolution HRTEM image of nanocrystals that form in the silica-rich passivating layers during mineral carbonation. The olivine host crystal is in the upper right of the image.



High resolution image of $MgCO_3$ and MgO nanocrystals observed in the disordered silica-rich passivating layer. $MgCO_3$ decomposes in the electron beam to give the MgO particles observed.

* Unstirred carbonation

CONCEPTUAL MODEL OF PASSIVATING LAYER FORMATION, STRUCTURE AND STRAIN STATE



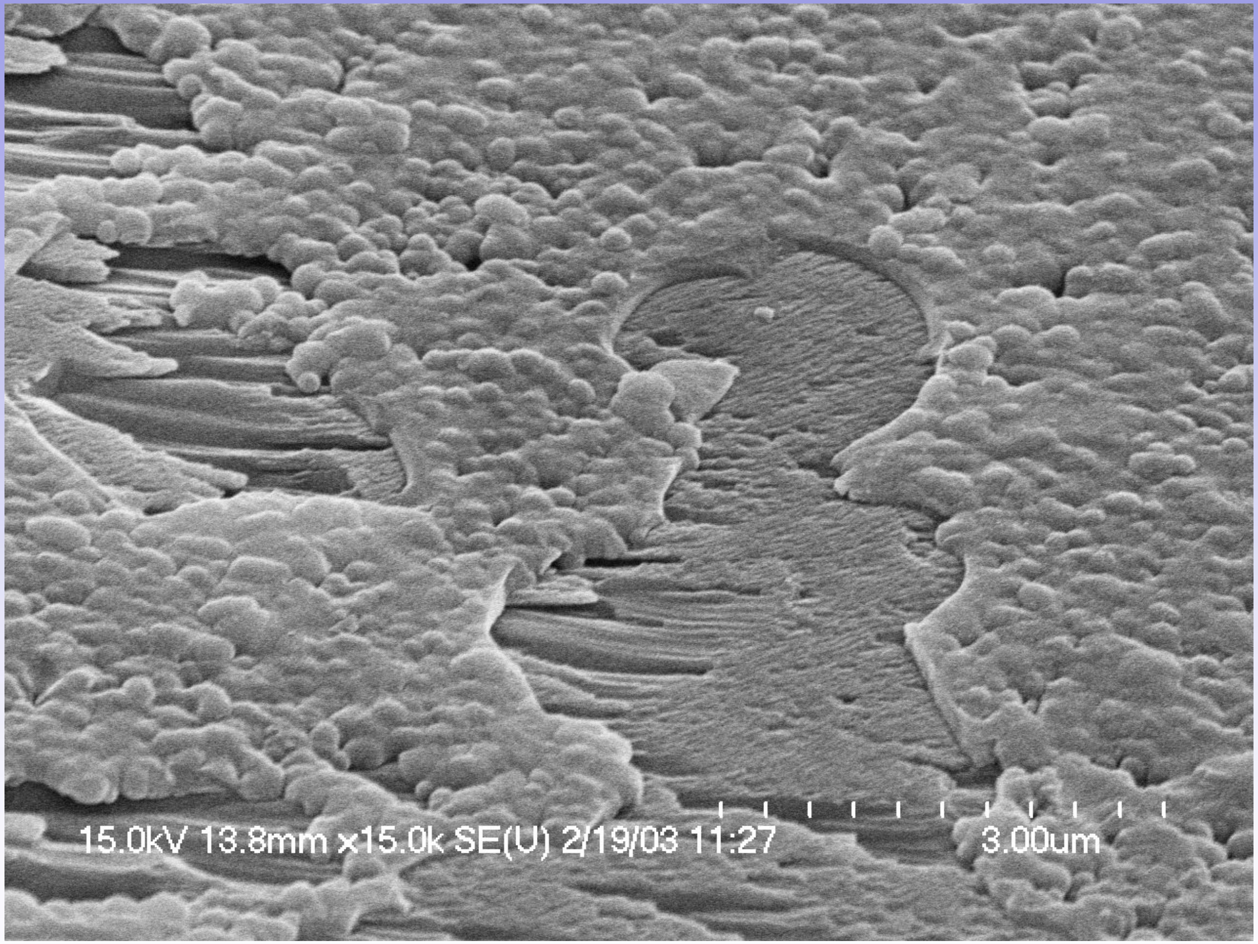
Schematic of the passivating layer formation process

$\%MgCO_3$ free	$\%MgCO_3$ In layer	V(products) / V(reactants)	Strain State of layer	$MgCO_3$ % Volume in layer
0%	100%	1.91	compression	67 %
10%	90%	1.78	compression	65 %
20%	80%	1.65	compression	62 %
30%	70%	1.52	compression	59 %
40%	60%	1.39	compression	55 %
50%	50%	1.26	compression	51 %
60%	40%	1.13	compression	45 %
70%	30%	1.01	compression	38 %
80%	20%	0.88	tension	29 %
90%	10%	0.75	tension	17 %*
100%	0%	0.62	tension	0%

* HRTEM

Calculated strain state of the passivating layer based on bulk molar volume data

SILICA-RICH PASSIVATING LAYER EXFOLIATION: ABRASIVE REMOVAL AND REGROWTH



***1,500 rpm stirring**

CAN CARBONATION BE ENHANCED BY CONTROLLING PASSIVATING LAYER FORMATION/EXFOLIATION?

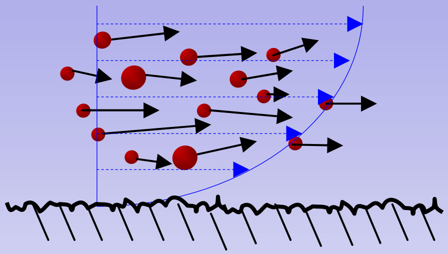
Objective: **to identify key parameters that can enhance olivine carbonation, while avoiding the cost of pretreatment activation.**

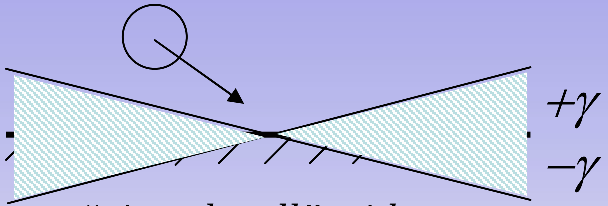
***Approaches include*:**

- **multi-phase fluid flow modeling and experimental investigations that elucidate key fluid-flow parameters and slurry interactions that can enhance exfoliation,**
- **chemical studies that probe the potential aqueous ion size and concentration (e.g., Li^+, Na^+, and K^+) offer to mitigate passivating layer effectiveness and enhance exfoliation, and**
- **investigations that elucidate the potential that cost effective sonication offers to enhance exfoliation and particle cracking.**

FLOW MODELING - APPROACH

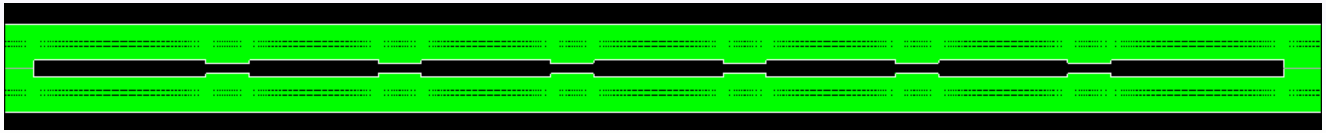
- **“Microscopic”…**
  - Modeling particle-particle and particle-wall interactions in simplified systems that enable detailed examination of specific processes.





“virtual wall” with random orientation, γ

- **“Macroscopic”…**
  - Engineering system prediction used to assess state-of-the-art and perform parametric tests integrated with experimental observations.
    - Extension of models for prediction of quantities such as mean pressure distributions, solids concentration, system flow, etc.

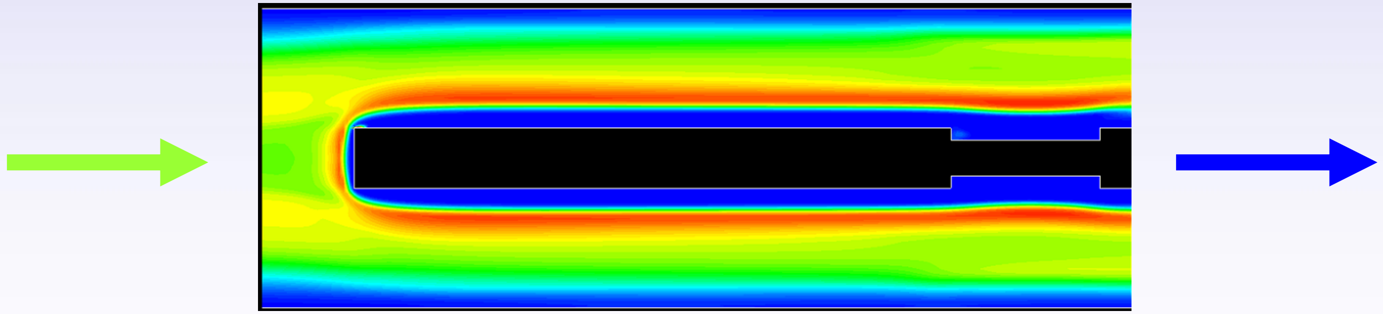


Pipe geometry with embedded mixer

FLOW MODELING – INITIAL STUDIES

- ***"Microscopic" modeling***
  - Developed and tested a new stochastic approach for modeling wall roughness
    - Strong effects of wall roughness are possible, potentially contributing to large increases in particle cross-stream transport and exfoliation.

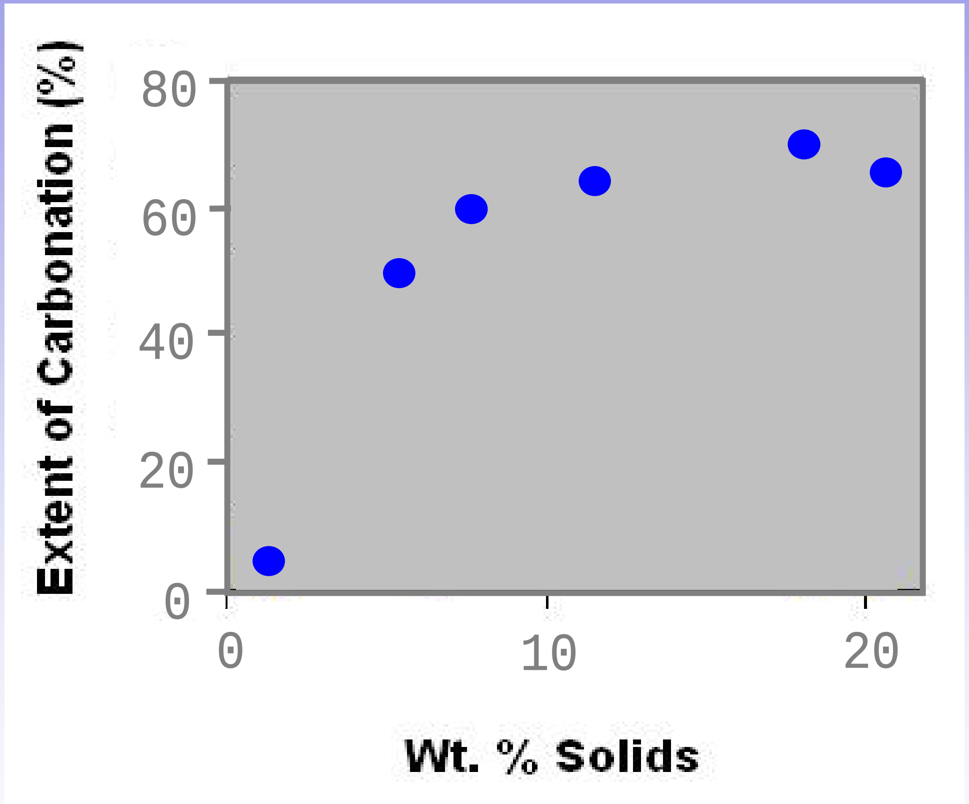
- ***"Macroscopic" modeling***
  - Integration of modeling with experimental studies using the flow loop reactor at the Albany Research Center. Prediction of average reactor flow properties and modifications that may enhance exfoliation/carbonation.
    - Mean pressure, velocity distributions, phase distributions at critical sections (joints, bends, elbows, flow mixer parts, etc.).



Olivine concentration around flow mixer (highest/red to lowest/blue)

Particle size distribution and concentration may critically impact carbonation

EFFECT OF PARTICLE CONCENTRATION ON CARBONATION



* Carbonation of synthetic olivine (Mg_2SiO_4) @ 185 ºC, 150 atm CO_2, with 1,500 rpm stirring for 1hr (ASU).

EFFECTS OF PARTICLE SIZE DISTRIBUTION AND SLURRY DENSITY

Experimental tests underway at ARC and ASU

Initial Studies of the Effect of Pump Speed and Particle Size On Olivine Carbonation in the ARC Flow Loop Reactor

Pump Speed (rpm)	Particle Size Fraction	Extent of Carbonation
1198	< 400 mesh (baseline)	72.0%
1002	< 200 mesh	66.9%
1198	< 200 mesh	63.2%
1450	< 200 mesh	73.8%
1750	< 200 mesh	77.9%

ARC Flow Loop Reactor

Initial observations

- **Carbonation remains high for < 200 mesh feedstock: potential for greatly reduced feedstock grinding costs.**
- **Increasing from 15 wt% to 30 wt% solids for < 200 mesh feedstock may slightly enhance carbonation, further reducing process cost.**
- **The presence of larger feedstock or inert (e.g., quartz) particles can enhance carbonation of smaller feedstock particles via increased abrasion.**

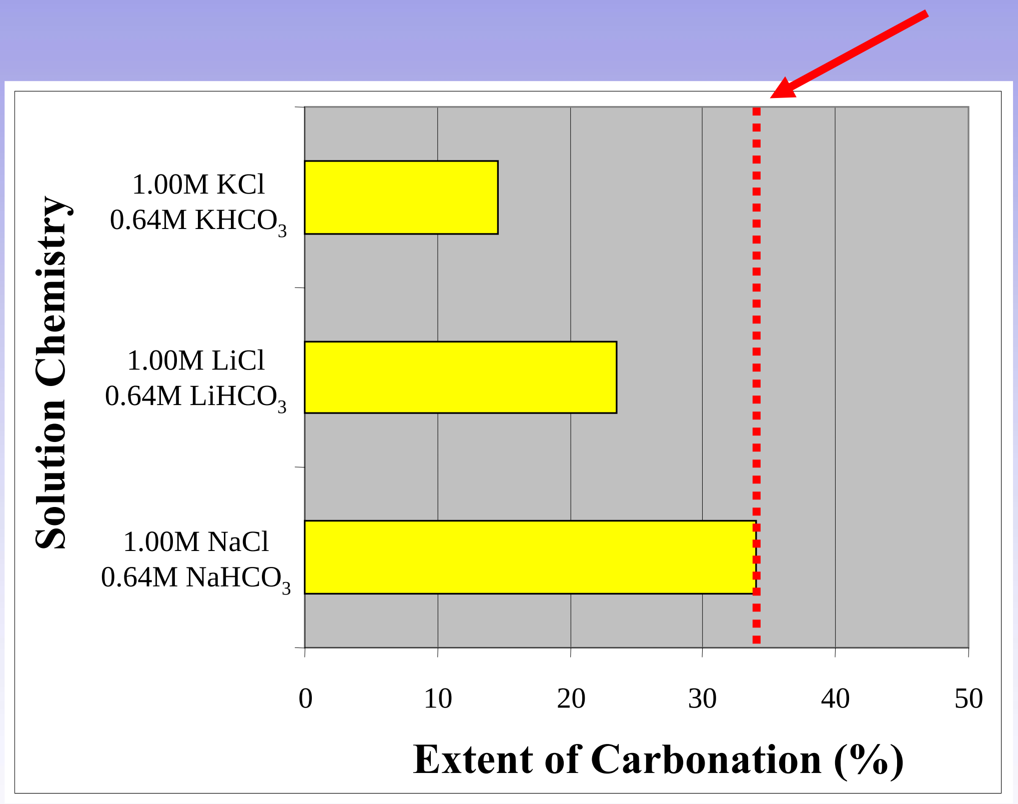
MULTIPHASE FLUID FLOW MODELING AND EXPERIMENTAL INVESTIGATIONS

FUTURE PLANS

- **Further explore the role of the particle concentration and size distribution and integrate findings into the simulations.**
- **Explore the influence of mixers and flow rate on flow field properties and carbonation.**
- **Incorporate insight gained from microscopic simulations of particle-particle and particle-wall collisions into phenomenological models for macroscopic simulations.**

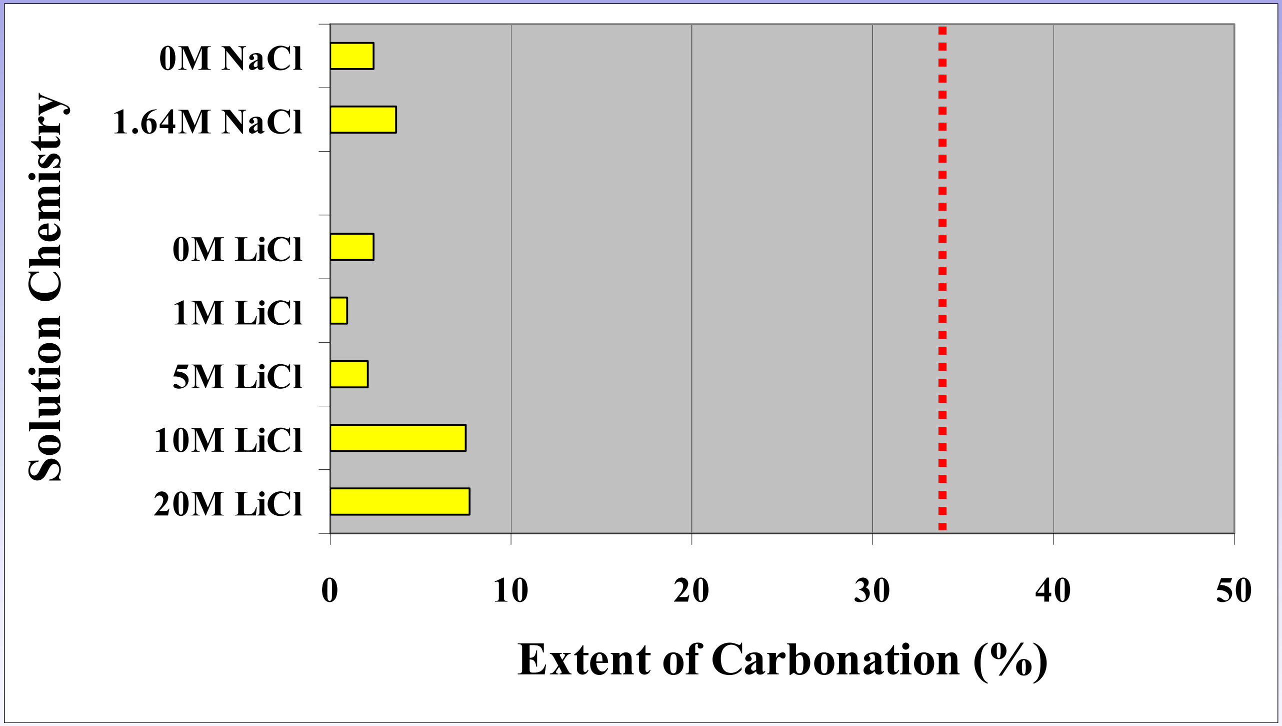
SOLUTION CHEMISTRY*: EFFECT OF ALKALI CATION SPECIES ON CARBONATION $A^+ = Na^+$, Li^+, or K^+

Comparison with the Optimum ARC Solution: 0.64M $NaHCO_3$ + 1.00M NaCl

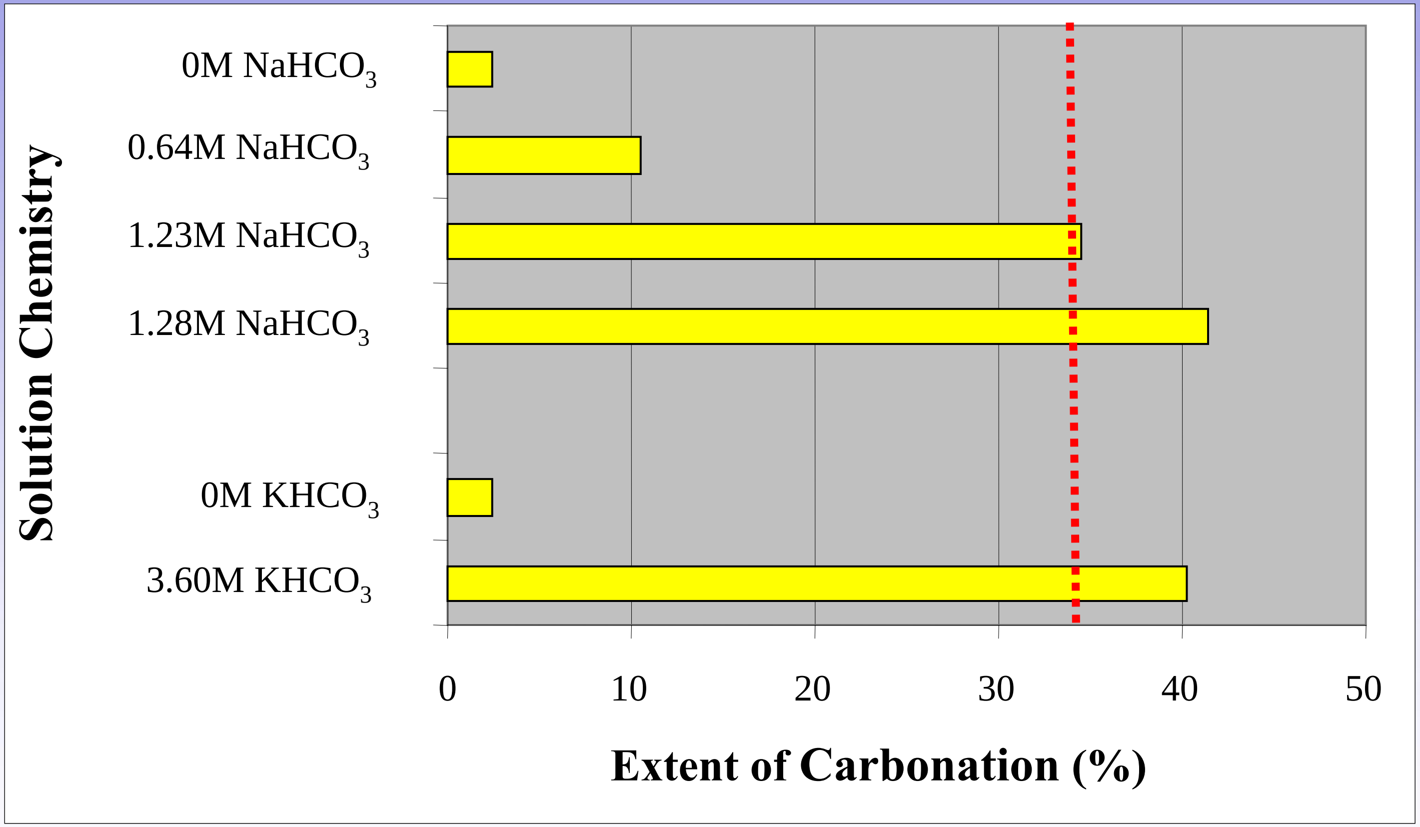


* **Note: Solution chemistry studies use single crystal San Carlos olivine fragments and the ASU batch reactor to explore the reaction products and mechanisms. This reaction combination exhibits significantly lower carbonation compared with the prior ARC Flow Loop Reactor carbonation of Twin Sisters olivine.**

SOLUTION CHEMISTRY: EFFECT OF ALKALI CHLORIDE SPECIES AND CONCENTRATION ON CARBONATION

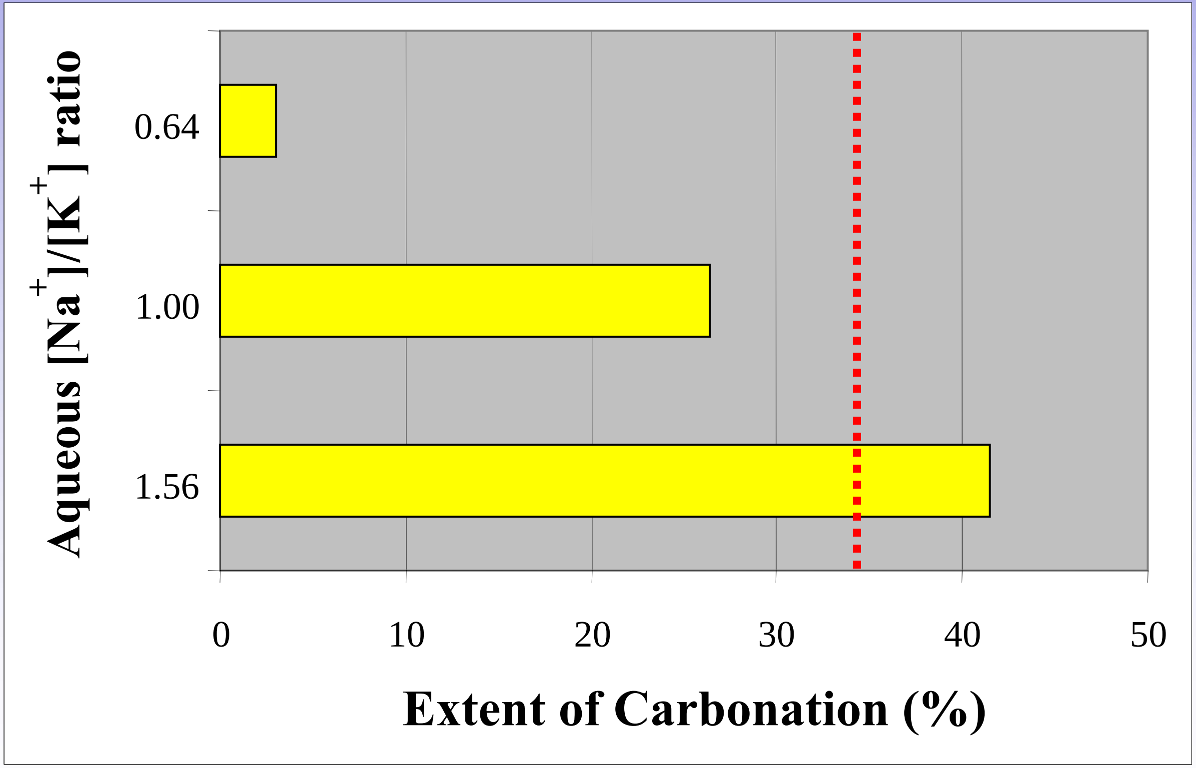


SOLUTION CHEMISTRY: EFFECT OF ALKALI BICARBONATE SPECIES AND CONCENTRATION ON CARBONATION



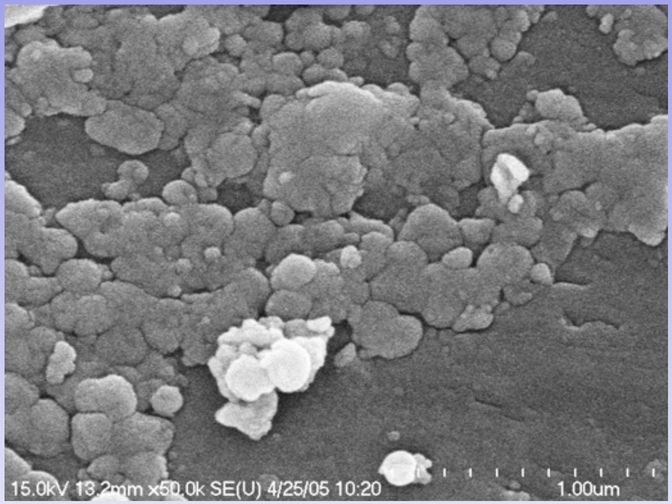
SOLUTION CHEMISTRY: EFFECT OF ALKALI CATION RATIO ON CARBONATION REACTIVITY

Comparison using the optimum ARC aqueous anion concentrations:
0.64M HCO_3^- + 1.00M Cl^-

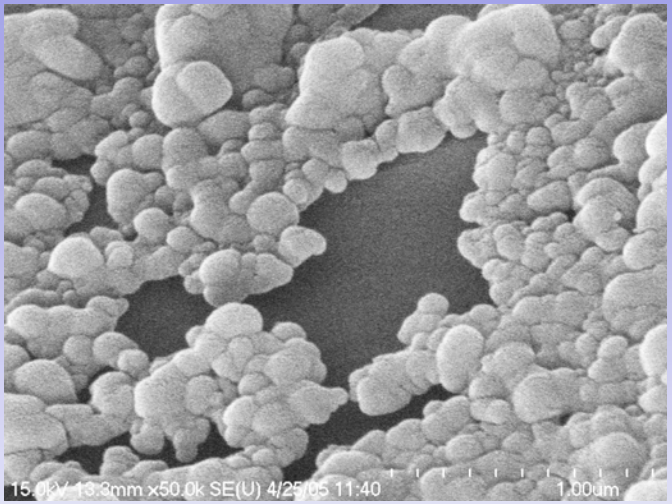


PRELIMINARY STUDY OF THE EFFECTS OF SONICATION ON CARBONATION REACTIVITY

Passivating Layer Formation during Carbonation



with 10 min. sonication



without sonication

Preliminary studies have shown no significant improvement in carbonation by incorporating relatively brief sonication.

- **sonication does not significantly break apart the olivine particle cores during carbonation.**
- **sonication can disrupt passivating layers, but they can readily regrow.**

Studies are continuing as a function of P, T, fluid composition, wt% solids, etc.

INITIAL CONCLUSIONS
(PROJECT 3RD QUARTER)

- **Controlling multiphase fluid flow offers intriguing potential to reduce process cost by enhancing passivating layer exfoliation *in situ* during carbonation.**

- **Controlling the alkali bicarbonate/chloride solution chemistry offers significant potential to enhance carbonation.**

- **Preliminary studies have not yet found evidence that controlled sonication can significantly enhance carbonation.**